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Attached herewith, is an official English translation of WO 01/48086 cited as prior art in the office actions dated 10/19/05 and 6/21/06.

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FLAME-RETARDANT RESIN COMPOSITION  
[Nannensei Jushi Soseibutsu]

Hatsuhiko Harashina, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
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## SPECIFICATION

/1\*

### FLAME-RETARDANT RESIN COMPOSITION

#### TECHNICAL FIELD

The present invention relates to flame retardant resin compositions that contain polyalkylene terephthalate resins.

#### RELATED ART

Polyalkylene terephthalate resins, such as polybutylene terephthalate and the like, have excellent mechanical and electrical properties, weather resistance, water resistance, and resistance to chemicals and solvents. Accordingly, they are used as engineering plastics in a variety of applications, including electric and electronic components, mechanical device components, and automotive parts. As their field of application expands, these resins are required to be flame-retardant from the viewpoint of safety. To impart flame retardancy to these resins, it is a common practice to add flame retardants comprised of halogen compounds or antimony compounds to these resins.

In JP-A-H10-168297 are disclosed flame-retardant resin compositions that are comprised of a thermoplastic polyester resin, polycarbonate resin, and phosphate-based organophosphorus flame retardant. In JP-A-H10-195283 are disclosed polyester resin compositions that are made flame-retardant by combining a phosphate having a specific structure, a novolak-type phenol resin, and an oxide

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\* Numbers in the margin indicate pagination in the foreign text.

of a specific metal, such as iron, cobalt, nickel, or copper, in suitable amounts. However, phosphate-based flame retardants, though do not contain harmful halogens, have flame retardancy inferior to that of halogen-based flame retardants and, as a result, need to be used in large quantities. Consequently, these resins have bleed-out problems and deterioration of their mechanical properties, and flame retardancy and mechanical properties cannot be improved concurrently.

In JP-A-H11-181268 is disclosed that the addition of 1.5 to 15 parts by weight of a phosphazene compound and 0.5 to 30 parts by weight of talc and/or mica to 100 parts by weight of a resin mixture containing an aromatic polycarbonate resin and a thermoplastic polyester resin in a proportion of from 90/10 to 50/50 (weight ratio) renders the resin mixture flame-retardant. However, aromatic /2  
polycarbonate-based resin compositions have a problem in solvent resistance, and they also exhibit poor melt flowability in the forming process, thus having poor formability.

In JP-A-H11-181429, specific phosphazene compounds (for example, cyclic phosphazene compounds, linear phosphazene compounds, crosslinked phosphazene compounds obtained by crosslinking the cyclic and/or linear phosphazene compounds with specific groups) are used as flame retardants to impart flame retardancy to either thermoplastic resins (for example, polyethylene terephthalate, polybutylene terephthalate, polycarbonate, and the like) or thermosetting resins (for example, phenol resin and the like). However, in the case of

imparting flame retardancy to polyethylene terephthalate or polybutylene terephthalate, the aforesaid phosphazene compounds alone cannot impart a satisfactory degree of flame retardancy to them.

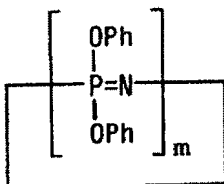
Accordingly, the present invention intends to provide polyalkylene terephthalate resin compositions that are rendered highly flame-retardant without deteriorating the properties of the resins.

#### DISCLOSURE OF INVENTION

The present inventors conducted extensive research to achieve the aforesaid objective and, as a result, found that a flame retardant comprising a combination of a phenoxyphosphazene compound and a phenol resin can render a polyalkylene terephthalate resin highly flame-retardant without deteriorating its mechanical properties. The present invention was accomplished based on this finding.

That is, the flame-retardant resin compositions of the present invention comprise a flame retardant containing a phosphazene compound and phenol resin and a polyalkylene terephthalate resin (for example, polyethylene terephthalate resin, polybutylene terephthalate resin, and so forth). The phosphazene compound comprises (1) a cyclic phenoxyphosphazene compound, (2) a linear phenoxyphosphazene compound, (3) a crosslinked phenoxyphosphazene compound, or the like.

(1) Cyclic phenoxyphosphazene compounds

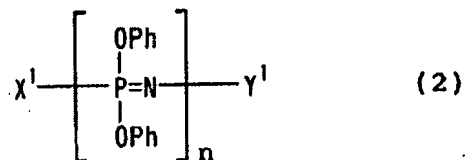


(1)

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(wherein m is an integer of 3 to 25, and Ph denotes a phenyl group.)

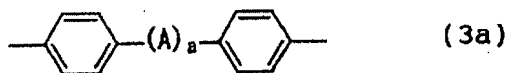
(2) Linear phenoxyphosphazene compounds



[wherein  $\text{X}^1$  represents the group  $-\text{N}=\text{P}(\text{OPh})_3$  or the group  $-\text{N}=\text{P}(\text{O})\text{OPh}$ ;  $\text{Y}^1$  represents the group  $-\text{P}(\text{OPh})_4$  or the group  $-\text{P}(\text{O})(\text{OPh})_2$ ; n is an integer of 3 to 10,000; and Ph has the same meaning as defined for the aforesaid formula 1.]

(3) Crosslinked phenoxyphosphazene compounds

Compounds that are formed by crosslinking a minimum of one kind of phenoxyphosphazene compound selected from the cyclic phenoxyphosphazene compounds (1) and linear phenoxyphosphazene compounds (2) with a minimum of one kind of crosslinking group selected from a group consisting of an o-phenylene group, m-phenylene group, p-phenylene group, and bisphenylene group that is represented by formula 3a:



[wherein A represents  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{SO}_2-$ ,  $-\text{S}-$ , or  $-\text{O}-$ , and a denotes 0 or 1], the proportion of said crosslinking groups being, in terms of the phenyl groups, 0.1 to 50 mol % based on the total number of the phenyl groups in the phenoxyphosphazene compounds (1) and (2).



The aforesaid phenol resin may be a phenol novolak resin, phenol aralkyl resin, polyvinyl phenol resin, or the like. The aforesaid flame retardant may contain the phosphazene compound and the phenol resin in a proportion of the former/the latter=5/95 to 95/5 (weight ratio) or thereabouts. The proportion of the flame retardant is from 1 to 100 parts by weight or thereabouts per 100 parts by weight of the polyalkylene terephthalate resin. The resin composition may further contain nitrogen-containing flame retardants (for example, melamine or 4 derivatives thereof, melamine condensates, cyanurates of melamine or its derivatives, and salts of pyrophosphoric acid or polyphosphoric acid with triazine derivatives), phosphate-based flame retardants (for example, phosphate, polyphosphate, and the like), carbonizable resins (for example, polycarbonate resin, polyarylate resin, aromatic epoxy resin, polyphenylene oxide resin, polyphenylene sulfide resin, and the like), antioxidants, thermal stabilizers, drip inhibitors, fillers, and so forth.

The flame-retardant resin compositions can be prepared by mixing a polyalkylene terephthalate resin and the aforesaid flame retardant.

The present invention also encompasses molded articles that are formed from the aforesaid flame-retardant resin compositions.

#### BEST MODE FOR IMPLEMENTING THE INVENTION

##### [Polyalkylene Terephthalate Resin]

The polyalkylene terephthalate resin includes homopolyesters and copolyesters that contain an alkylene terephthalate as the main

component (for example, about 50 to 100% by weight, preferably about 75 to 100% by weight.) Examples of the homopolyesters include poly 1,4-cyclohexane dimethylene terephthalate (PCT), polyethylene terephthalate (PET), polypropylene terephthalate (PPT), polybutylene terephthalate (PBT), and so forth. Examples of the copolymerizable monomers of the copolyesters include alcohol components, such as (poly)ethylene glycol, (poly)propylene glycol, and (poly)butylene glycol; carboxylic acid components, such as adipic acid, sebacic acid, isophthalic acid, naphthalene dicarboxylic acid, biphenylene dicarboxylic acid, hydroxycarboxylic acid, and hydroxynaphthoic acid; and so forth. These polyalkylene terephthalates can be used singly or in combination of two or more kinds. Preferable polyalkylene terephthalate resins are polyethylene terephthalate resin, polypropylene terephthalate resin, polybutylene terephthalate resin, and the like. Among these, poly C<sub>2-4</sub> alkylene terephthalates, such as polyethylene terephthalate, polybutylene terephthalate, and the like, are especially desirable.

The number-average molecular weight of the polyalkylene terephthalate resin is not specifically limited and can be selected from the range of, for example, from  $5 \times 10^3$  to  $100 \times 10^4$ , preferably from  $1 \times 10^4$  to  $70 \times 10^4$ , better yet, from  $1.2 \times 10^4$  to  $30 \times 10^4$ .

The polyalkylene terephthalate resin is prepared by a conventional method--for example, a transesterification method or a

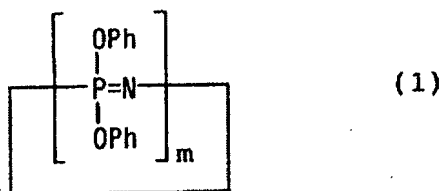
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direct esterification method with use of alkylene glycol and terephthalic acid.

[Flame retardant]

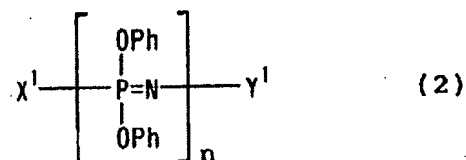
The flame retardant of the present invention is comprised of a phosphazene compound (a cyclic phenoxyphosphazene compound, linear phenoxyphosphazene compound, crosslinked phenoxyphosphazene compound, or the like) and a phenol resin. Forming a flame retardant from a phosphazene compound and a phenol resin makes it possible to impart high flame retardancy to polyalkylene terephthalate resins without deteriorating their mechanical properties.

Examples of the cyclic phenoxyphosphazene compound include compounds represented by the following formula (1):



(wherein m is an integer of 3 to 25, and Ph denotes a phenyl group.)

Examples of the linear phenoxyphosphazene compound include compounds represented by the following formula (2):



[wherein X<sup>1</sup> represents the group -N=P(OPh)<sub>3</sub> or the group -N=P(O)OPh; Y<sup>1</sup> represents the group -P(OPh)<sub>4</sub> or the group -P(O)(OPh)<sub>2</sub>; n is an

integer of 3 to 10,000; and Ph has the same meaning as defined for the aforesaid formula 1.]

Examples of the crosslinked phenoxyphosphazene compound include compounds that are formed by crosslinking a minimum of one kind of phenoxyphosphazene compound selected from the cyclic phenoxyphosphazene compounds (1) and linear phenoxyphosphazene compounds (2) with a divalent crosslinking group. Incidentally, when a pair of phenoxyphosphazene compounds is crosslinked with the aforesaid crosslinking group, the divalent crosslinking group is introduced to take the place of a pair of Ph groups. /6

Examples of the divalent crosslinking group include phenylene groups (such as an o-phenylene group, m-phenylene group, and p-phenylene group) and bisphenylene groups that are represented by formula 3a below:



[wherein A represents  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{SO}_2-$ ,  $-\text{S}-$ , or  $-\text{O}-$ , and a denotes 0 or 1]. These crosslinking groups may be used singly or in combination of two or more kinds.

The proportion of the crosslinking groups is, in terms of the phenyl groups, 0.1 to 50 mol % based on the total number of the phenyl groups in the phenoxyphosphazene compounds (1) and (2).

It is preferable that the crosslinked phenoxyphosphazene compounds do not, in essence, contain free hydroxyl groups in the molecules.

These phosphazene compounds may be used singly or in combination of two or more.

The cyclic and linear phenoxyphosphazene compounds represented by the formulas (1) and (2) can be synthesized by, for example, the methods described in "Phosphorus-Nitrogen Compounds" by H. R. Allcock, published by Academic Press, (1972) and in "Inorganic Polymers" by J. E. Mark, H. R. Allcock, and R. West, published by Prentice-Hall International, Inc., (1992).

For example, phosphorus chloride (for example, phosphorus trichloride, phosphorus pentachloride, or the like), ammonium chloride, and, if necessary, chlorine (in particular, in the case of using phosphorus trichloride as the phosphorus chloride) are reacted in a chlorine-based solvent (for example, chlorobenzene, tetrachloroethane, or the like), thereby obtaining a mixture of a compound (a cyclic dichlorophosphazene oligomer) represented by a formula that has chlorine atoms (Cl) in place of the OPh groups of formula (1) and that has an integer of 3 to 25 as the "m" of the same formula and a compound (a linear dichlorophosphazene oligomer) represented by a formula that has chlorine atoms (Cl) in place of the OPh groups of formula (2) and that has an integer of 3 to 25 as the "n" in the same formula. The cyclic and linear phenoxyphosphazene compounds

represented by formulas (1) and (2) can be obtained by substituting the 7 chlorine atoms of this dichlorophosphazene oligomer mixture by phenol with the use of an alkali metal phenolate (for example, sodium phenolate or the like).

The reaction temperature in the reaction of phosphorus chloride and ammonium chloride is, for example, from 120 to 130°C or thereabouts.

If necessary, the dichlorophosphazene oligomer mixture may be subjected to purification (for example, distillation, recrystallization, or the like) or polymerization (ring-opening polymerization of the cyclic dichlorophosphazene oligomer). By purifying the dichlorophosphazene oligomer mixture, a single or sole compound of the cyclic dichlorophosphazene (for example, hexachlorocyclotriphosphazene, octachlorocyclotetraphosphazene, decachlorocyclopentaphosphazene, and the like) can be obtained. Therefore, by substituting this single compound with a phenol, the cyclic phenoxyphosphazene compound, such as hexaphenoxycyclotriphosphazene, octaphenoxycyclotetraphosphazene, and decaphenoxycyclopentaphosphazene, can be obtained.

On the other hand, ring-opening polymerization of the cyclic dichlorophosphazene oligomer yields a compound that is represented by a formula that has chlorine atoms in place of the OPh groups of formula (2) and that has an integer of 3 to 10,000 as the "n" of the same formula. Therefore, by substituting this compound with phenol,

the linear phenoxyphosphazene compounds represented by formula (2) can be obtained.

The ring-opening polymerization of the cyclic dichlorophosphazene oligomer can be implemented by, for example, heating the oligomer to 220 to 250°C.

The crosslinked phenoxyphosphazene compound can be produced by the partial substitution (crosslinking) of the chlorine atoms of the dichlorophosphazene oligomers with an alkali metal salt of an aromatic dihydroxy compound instead of substituting the entire chlorine atoms with an alkali metal salt of phenol in the production process of the cyclic phosphazene compound (1) or the linear phosphazene compound (2).

The dichlorophosphazene oligomers used here are not particularly limited and may be a mixture of the cyclic dichlorophosphazene oligomer and the linear dichlorophosphazene oligomer, or these may be used individually. The order of the reactions is also not particularly 8 limited. For example, an alkali metal salt of phenol and an alkali metal salt of an aromatic dihydroxy compound may be mixed and then used for the reaction. Alternatively, the oligomers may be reacted with an alkali metal salt of phenol and subsequently with an alkali metal salt of an aromatic dihydroxy compound or vice versa.

However, it is more desirable to employ the following method. The aforesaid dichlorophosphazene compound (cyclic dichlorophosphazene oligomer, linear dichlorophosphazene oligomer, and the like), an alkali metal salt of phenol, and an alkali metal salt of an aromatic

dihydroxy compound are reacted (the first stage reaction), thereby obtaining a partially substituted compound in which part of the chlorine atoms of the dichlorophosphazene compound is substituted by phenol, part thereof is substituted by the aromatic dihydroxy compound, and part thereof remains as chlorine atoms. Thereafter, this partially substituted compound is reacted with an alkali metal salt of phenol (the second stage reaction), thereby obtaining a crosslinked phenoxyphosphazene compound. In the crosslinked phenoxyphosphazene compound obtained in this manner, there are essentially no free hydroxyl groups remaining since all of the hydroxyl groups of the aromatic dihydroxy compound are reacted with the dichlorophosphazene compound.

As the aromatic dihydroxy compound, the present invention can use a compound having one or more benzene rings in the molecule and two hydroxyl groups, more concretely, a compound having the crosslinking groups described before (an o-phenylene group, m-phenylene group, p-phenylene group, and a group represented by formula 3a). Preferable examples of the aromatic dihydroxy compound include resorcinol, hydroquinone, catechol, 4,4'-isopropylidenediphenol (bisphenol-A), 4,4'-sulfonyldiphenol (bisphenol-S), 4,4'-thiodiphenol, 4,4'-oxydiphenol, 4,4'-diphenol, and the like. These aromatic dihydroxy compounds can be used singly or in combination of two or more kinds.



Examples of the alkali metal that constitutes the alkali metal salt include sodium, potassium, lithium, and the like, of which sodium and lithium are preferable.

In the first stage reaction, the total amount of the alkali metal salts of phenol and the aromatic dihydroxy compound is usually about 0.05 to 0.9 equivalent, preferably about 0.1 to 0.8 equivalent, based /9 on the chlorine content of the dichlorophosphazene oligomers. When the amount of the alkali metal salts used is less than 0.05 equivalent, the degree of the crosslinking becomes insufficient. On the other hand, when the amount of the alkali metal salts exceeds 0.9 equivalent, a free hydroxyl group (a hydroxyl group at one end of the dihydroxy compound) is introduced into the crosslinked phenoxyphosphazene compound.

The ratio of the alkali metal salt of the aromatic dihydroxy compound to that of phenol is not particularly limited and can be suitably selected from a wide range, but it is usually in the range of the former/the latter=1/2000 to 1/4 (molar ratio) or thereabouts. When the ratio is considerably smaller than 1/2000, the degree of the crosslinking becomes insufficient. On the other hand, a ratio that is considerably larger than 1/4 causes the crosslinking reaction to proceed excessively; as a result, the solubility and meltability of the resulting crosslinked phenoxyphosphazene compound deteriorate, and its dispersibility in a resin becomes insufficient.

The first and second stage reactions may be carried out in a solvent (for example, in an aromatic hydrocarbon, such as benzene, toluene, xylene, or the like, or in a halogenated aromatic hydrocarbon, such as chlorobenzene or the like).

The reaction temperature is usually from room temperature (for example, 15 to 30°C or thereabouts) to 150°C or thereabouts.

In the second stage reaction, the amount of the alkali metal salt of phenol is usually about 1 to 1.5 equivalent, preferably about 1 to 1.2 equivalent, based on the chlorine content of the dichlorophosphazene oligomers.

The proportion of the phosphazene compound is, for example, from 1 to 40 parts by weight, preferably from 1 to 30 parts by weight, better yet, from 5 to 25 parts by weight, or thereabouts per 100 parts by weight of the polyalkylene terephthalate resin.

As the phenol resin, the present invention may use various resins that have a phenol residue as a constituent unit. Some examples thereof include novolak resins, aralkyl resins, and polyvinyl phenol resins.

The novolak resins include phenol novolak resins obtained by the reaction (condensation reaction) of phenols (for example, phenol; C<sub>1-10</sub> alkyl group-substituted phenols, such as cresol, ethylphenol, propylphenol, butylphenol, and octylphenol; cyanophenol; and so forth) and aldehydes (for example, formaldehyde, acetaldehyde,

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propionaldehyde, and the like, of which formaldehyde is especially suitable).

The aforesaid condensation reaction of phenols and aldehydes may be carried out in the presence of an acid catalyst, such as an inorganic acid (for example, hydrochloric acid, sulfuric acid, or the like) or an organic acid (for example, p-toluenesulfonic acid, oxalic acid, or the like), or may be carried out in the absence of a catalyst. The ratio of phenols to aldehydes is the former/the latter=1/0.6 to 1/1 (molar ratio) or thereabouts.

The aforesaid phenol novolak resins also include random phenol novolak resins, in which methylene bonds randomly with phenolic hydroxyl groups; high-ortho phenol novolak resins, in which methylene bonding to phenolic hydroxyl groups occurs more often at the ortho position (for example, resins having an ortho/para ratio of 1 or larger); triazine-modified phenol novolak resins (for example, those obtained by copolycondensation of a triazine and a phenol novolak resin), which are modified with triazines (for example, melamine, benzoguanamine, and the like); and so forth. Further, phenol novolak resins that contain the free monomer component and dimer component only in small quantities [for example, resins in which the total amount of the free monomer and dimer components is not more than 20% by weight (for example, from 0 to 20% by weight or thereabouts) of the resin as a whole, preferably not more than 10% by weight (for example, from 0 to 10% by weight or thereabouts), better yet, not more than 5 %

by weight (for example, from 0 to 5 % by weight or thereabouts)] are also desirable.

The aralkyl resins include phenol aralkyl resins obtained by the reaction of the phenols exemplified in the section pertaining to the novolak resins with aralkyls (reactive compounds having a xylylene unit--for example, xylylene glycols or derivatives thereof, such as p-xylylene glycol,  $\alpha,\alpha'$ -dimethoxy-p-xylene, and the like, and  $\alpha,\alpha'$ -dihalo-p-xylene, such as  $\alpha,\alpha'$ -dichloro-p-xylene and the like).

The polyvinyl phenol resins include homopolymers of vinyl phenol and copolymers of vinyl phenol with other copolymerizable monomers [for example, styrenes, such as styrene, vinyl toluene, and  $\alpha$ -methylstyrene; (meth)acrylic acids or derivatives (for example, esters, acid amides, and so forth) thereof, such as (meth)acrylic acids and /11 (meth)acrylates; (meth)acrylonitriles; and so forth].

The phenol resins can be used singly or in combination of two or more kinds. The preferred phenol resins are phenol novolak resins, phenol aralkyl resins, homo- or copolymers of vinyl phenol.

A part or all of the phenolic hydroxyl groups of the phenol resins may be optionally modified with boric acid, borate, phosphoric acid, phosphate, or the like.

The number-average molecular weight of the phenol resin is not specifically limited and can be selected from the range of from 300 to  $5 \times 10^4$ , preferably from 300 to  $1 \times 10^4$ , better yet, from 300 to 8,000, or thereabouts.

The ratio of the phenol resin used in the flame retardant is, for example, about 1 to 40 parts by weight, preferably about 1 to 30 parts by weight, better yet, about 3 to 25 parts by weight (about 5 to 20 parts by weight is particularly suitable), per 100 parts by weight of the polyalkylene terephthalate resin.

The ratio of the phosphazene compound to the phenol resin in the flame retardant is, for example, the former/the latter=about 5/95 to 95/5 (weight ratio), preferably about 20/80 to 80/20 (weight ratio), better yet, about 30/70 to 70/30 (weight ratio).

Since the flame retardant of the present invention contains a phenol resin, it can impart flame retardancy to polyalkylene terephthalate resins while inhibiting the decrease of the molecular weight and mechanical properties (for example, strength, impact resistance, and so forth) of the polyalkylene terephthalate resins. The use of the phosphazene compound and the phenol resin in combination especially makes it possible to impart higher flame retardancy to the polyalkylene terephthalate resins compared with the case of using the phosphazene compound alone. Moreover, since the aforesaid flame retardant does not contain any halogen, it poses no risk of generating hydrogen halides, which is poisonous gas, upon decomposition or burning and of causing the corrosion of a mold and deterioration of the resin in the process of molding the resin.

The proportion of the flame retardant in the resin composition is not particularly limited as long as the properties of the polyalkylene terephthalate resin are not adversely affected, and it is about 1 to 100 parts by weight, preferably about 5 to 90 parts by weight (for 12 example, about 5 to 80 parts by weight), better yet, about 10 to 80 parts by weight (for example, about 20 to 60 parts by weight) per 100 parts by weight of the polyalkylene terephthalate resin. If the amount of the flame retardant is less than 1 part by weight, it is difficult to achieve flame retardancy, and an amount exceeding 100 parts by weight causes a molded article obtained from the resulting resin composition to have poor mechanical strength and moldability.

The polyalkylene terephthalate resin composition of the present invention may optionally contain other flame retardants, carbonizable resins, and additives [for example, drip inhibitors, antioxidants, stabilizers (such as thermal stabilizers and the like)]. The amount of other flame retardants contained in the composition is about 0 to 50 parts by weight, preferably about 1 to 30 parts by weight, better yet, about 3 to 20 parts by weight, per 100 parts by weight of the polyalkylene terephthalate resin. The amount of the carbonizable resin is about 0 to 100 parts by weight, preferably about 1 to 80 parts by weight, better yet, about 10 to 60 parts by weight, per 100 parts by weight of the polyalkylene terephthalate resin. The amount of the additives is about 0.01 to 20 parts by weight, preferably about 0.1 to

10 parts by weight, per 100 parts by weight of the polyalkylene terephthalate resin.

Examples of other flame retardants include nitrogen-containing flame retardants [for example, aminotriazines, such as melamine and guanamine; melamine condensates, such as melam and melem; cyanurates of aminotriazines, such as melamine cyanurate and guanamine cyanurate; salts of pyrophosphoric acid or polyphosphoric acid with triazine derivatives (such as a melamine salt, melam salt, melem salt, melamine·melam·melem complex salt, and the like), and so forth], organophosphorus flame retardants [phosphate-based flame retardants--for example, phosphates (such as triphenyl phosphate, tricresyl phosphate, and the like) and polyphosphates [polyphosphates having an aromatic ring, such as hydroquinone bis(diphenyl phosphate), hydroquinone bis(dicresyl phosphate), hydroquinone bis(dixylyl phosphate), biphenol bis(dixylyl phosphate), resorcinol bis(diphenyl phosphate), resorcinol bis(dicresyl phosphate), resorcinol bis(dixylyl phosphate), bisphenol-A bis(diphenyl phosphate), bisphenol-A bis(dicresyl phosphate), and bisphenol-A bis(dixylyl phosphate)], inorganic phosphorus flame retardants (for example, red phosphorus that may optionally be coated with a resin, phosphoric acid salts, and so forth), sulfur-containing flame retardants, silicon-containing flame retardants [such as (poly)organosiloxane and the like], boron-containing flame retardants (such as hydrated zinc borate and the like), inorganic flame retardants (such as metal oxides, metal

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hydroxides, and the like). These flame retardants can be used singly or in combination of two or more kinds.

Examples of the carbonizable resins include resins having an aromatic ring. As such aromatic ring-containing resins, there may be exemplified polycarbonate-based resins, polyarylate-based resins, aromatic epoxy resins (such as bisphenol-A-type epoxy resins, novolak-type epoxy resins, phenoxy resins, and the like), polyphenylene oxide-based resins, polyphenylene sulfide-based resins, and so forth. These carbonizable resins can be used singly or in combination of two or more kinds.

The use of the aforesaid other flame retardants (the nitrogen-containing flame retardants or phosphate-based flame retardants) and/or carbonizable resins in combination with the aforesaid specific flame retardants makes it possible to further improve the flame retardancy of the polyalkylene terephthalate resin.

The drip inhibitors include fluororesins (such as homo- or copolymers of fluorine-containing monomers and copolymers of the fluorine-containing monomers with other copolymerizable monomers), layered silicates, and so forth. Examples of such fluororesins include polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, tetrafluoroethylene-hexafluoropropylene copolymer, tetrafluoroethylene-perfluoroalkylvinylether copolymer, ethylene-tetrafluoroethylene copolymer, ethylene-chlorotrifluoroethylene copolymer, and the like.



Examples of antioxidants include hindered phenol-based antioxidants {such as 2,6-di-t-butyl-p-cresol, 2,2'-methylene bis(4-methyl-6-t-butylphenol), 2,2'-thiobis(4-methyl-6-t-butylphenol), 4,4'-thiobis(6-t-butyl-m-cresol), and pentaerythritol tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], and the like}, amine-based antioxidants (such as naphthylamine and the like), and phosphorus-/14  
based antioxidants {for example, phosphites [such as bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite, and the like], phosphonites [such as tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene diphosphonite and the like]}.

Examples of the thermal stabilizers include inorganic phosphorus-based stabilizers--for example, phosphoric acid, phosphorous acid, pyrophosphoric acid, tripolyphosphoric acid, primary alkali metal phosphates, primary alkali metal phosphate [sic] (such as primary sodium phosphate and the like), primary alkaline earth metal phosphates (such as primary calcium phosphate and the like), and so forth.

The resin composition of the present invention may further contain, as necessary, other additives, such as lubricants, plasticizers, flame retardant aids, ultraviolet absorbers, pigments, dyes, antistatic agents, dispersing agents, compatibilizers, antibacterial agents, and so forth.

Furthermore, the resin composition may optionally contain fillers (such as kaolin, mica, talc, calcium carbonate, titanium oxide, glass fiber, glass flake, glass bead, milled fiber, various metal foils, carbon fiber, and the like).

When a filler is used, the proportion of the filler in the flame-retardant resin composition is, for example, about 1 to 60% by weight, preferably about 5 to 50% by weight, better yet, about 5 to 45% by weight.

Furthermore, in the case of using a filler, a sizing agent or a surface-treatment agent may be optionally used. Examples of such a sizing agent or surface-treatment agent include functional compounds. The aforesaid functional compounds include epoxy-based compounds, silane-based compounds, titanate-based compounds, and so forth.

The resin composition of the present invention may be in the form of a powder mixture or melt mixture, and it is prepared by mixing the polyalkylene terephthalate resin, the above specific flame retardant, and optionally other flame retardants, carbonizable resins, additives, and so forth according to a conventional method.

The resin composition of the present invention can be melt-kneaded and molded by a conventional method, including extrusion molding, injection molding, and compression molding. Since the thus- /15 molded articles have excellent flame retardancy and moldability, they can be utilized in a variety of applications. For example, they may be

suitable for use as electric or electronic components, mechanical device components, and automotive parts.

#### INDUSTRIAL APPLICABILITY

Since the present invention employs a flame retardant that is prepared by combining the specific phosphazene compound and phenol resin, it becomes possible to impart flame retardancy to polyalkylene terephthalate resins without using any halogen-containing flame retardant. According to the present invention, the polyalkylene terephthalate resins can be rendered especially highly flame retardant without adversely affecting the inherent characteristics of the polyalkylene terephthalate resins even after flame retardancy is imparted to them.

#### WORKING EXAMPLES

The following will explain the present invention in further detail by referring to working examples, but these examples should not be construed as a limitation on the scope of the invention.

In Working Examples and Comparative Examples, the polyalkylene terephthalate resins, flame retardants (phosphazene compounds, phenol resins), and optionally other flame retardants, carbonizable resins, additives (antioxidants, thermal stabilizers, and drip inhibitors), and fillers that are presented below were used.

##### [Polyalkylene Terephthalate A]

A-1: polybutylene terephthalate [Duranex, intrinsic viscosity: 1.0, a product of Polyplastics, Co.]

A-2: polybutylene terephthalate [Duranex, intrinsic viscosity: 0.75, a product of Polyplastics, Co.]

A-3: polyethylene terephthalate (BelPet EFG10, a product of Kanebo, Ltd.)

[Phosphazene Compound B]

B-1 through B-5: phenoxyphosphazene compounds obtained in the following synthesis examples 1 through 5.

[Phenol resin C]

C-1: novolak resin [Tamanol 759, a product of Arakawa Chemical Industries, Ltd.] /16

C-2: novolak resin [Sumilite Resin PR-53195 (free monomer component: 0.3% by weight, dimer component: 17% by weight ), a product of Sumitomo Durez Co.]

C-3: novolak resin [Sumilite Resin PR-53647 (free monomer component: 0.03% by weight, dimer component: 1.6% by weight), a product of Sumitomo Durez, Co.]

C-4: phenol aralkyl resin [Milex XL-225, a product of Mitsui Chemicals, Inc.]

C-5: polyvinyl phenol [Maruka Lyncur-MS-1P, a product of Maruzen Petrochemical Co.]

C-6: novolak resin

After 500 parts by weight of phenol, 225 parts by weight of 37% formalin, and 5 parts by weight of oxalic acid were refluxed and reacted for 3 hours, the reaction system was distilled under an

ambient pressure and also under reduced pressure, thereby obtaining 350 parts by weight of a novolak-type phenol resin. The resulting resin was subjected to GPC [gel permeation chromatography], and the free monomer component and dimer component were found to be 0.3% by weight and 21% by weight, respectively.

[Other Flame retardant D]

D-1: melamine cyanurate [MC610, a product of Nissan Chemical Industries, Ltd.]

D-2: resorcinol bis(dixylyl phosphate) [PX200, a product of Daihachi Chemical Industry. Co.]

D-3: melam polyphosphate [PMP200, a product of Nissan Chemical Industries, Co.]

[Carbonizable Resin E]

E-1: polycarbonate [Panlite L1225, a product of Teijin Chemicals, Ltd.]

E-2: bisphenol A-type epoxy resin [Epikote 1004K, a product of Yuka Shell Epoxy K.K.]

[Antioxidant/Thermal Stabilizer F]

F-1: pentaerythritol tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] [Irganox 1010, a product of Ciba-Geigy Ltd.]

F-2: bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite /17  
[Adekastab PEP36, a product of Adeka Argus Co.]

F-3: tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene diphosponite  
[Sandostab P-EPQ, a product of Sando Co.]

F-4: primary calcium phosphate

[Drip Inhibitor G]

G-1: polytetrafluoroethylene

[Filler H]

H-1: glass fiber (diameter: 13  $\mu$ m, chopped strand of 3 mm in length)

H-2: glass fiber (diameter: 10  $\mu$ m, chopped strand of 3 mm in length)

Synthesis Example 1 (Synthesis of Cyclic Phenoxyphosphazene Compound B-1)

Reference: H. R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, (1972).

To 580 g of a 20% by weight chlorobenzene solution that contained 1.0 unit mol (115.9 g) of dichlorophosphazene oligomers (a mixture of 62% by weight of a trimer and 38% by weight of a tetramer) was added a toluene solution of sodium phenolate under stirring, and they were reacted for 4 hours at 110°C, thereby obtaining a cyclic phenoxyphosphazene compound. The amount of the hydrolyzed chlorine after purification was 0.08% by weight.

Synthesis Example 2 (Synthesis of Phenoxyphosphazene Compound B-2)

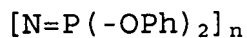
To a 1 L-capacity four-neck flask equipped with a stirrer, thermometer, and reflux condenser were added 1.3 mol (123.0 g) of phenol and 500 mL of tetrahydrofuran, and a homogeneous solution was formed. Subsequently, 27.6 g of metal sodium was added to the solution at 25°C or lower, and, after the addition, the solution was stirred

continuously for 6 hours at 61 to 68°C, thereby obtaining a sodium phenolate solution.

The aforesaid sodium phenolate solution was added drop by drop into a 2 L-capacity four neck flask that held 290 g of a 20% by weight chlorobenzene solution that contained 0.5 unit mol (58 g) of dichlorophosphazene oligomers (a mixture of 59% by weight of a trimer, 12% by weight of a tetramer, 11% by weight of a pentamer and hexamer, 3% by weight of a heptamer, and 15% by weight of oligomers having /18 eight or more repeating units) under stirring at 25°C or lower. After the addition, the mixture was stirred and reacted for 15 hours at 71 to 73°C. After the completion of the reaction, the reaction mixture was condensed and redissolved in 500 mL of chlorobenzene, after which it was washed three times with a 5% by weight NaOH aqueous solution, washed with 5% by weight sulfuric acid, washed with a 5% by weight sodium hydrogen carbonate aqueous solution, washed twice with water, and condensed to dryness, thereby obtaining 108 g of a light yellow wax-like product.

The product was analyzed by GPC and found to have a weight-average molecular weight (Mw) of 810, in terms of polystyrene equivalent. It was further analyzed by TG/DTA [Thermogravimetry-Differential Thermal Analysis], and its melting temperature was found to be 103°C; decomposition initiating temperature, 330°C; and 5% weight-loss temperature, 347°C. Furthermore, the amount of the residual chlorine (the hydrolyzed chlorine: Hy-Cl) was 0.09% by weight,

and, by the elemental analysis of phosphorus and CHN, it was determined that the product was the following compound.



Synthesis Example 3 (Synthesis of Phenoxyphosphazene Compound B-3 Having a Crosslinking Structure with the Use of m-phenylene)

A mixture of 1.1 mol (103.5 g) of phenol, 1.1 mol (44.0 g) of sodium hydroxide, 50 g of water, and 500 mL of toluene was heated and refluxed, and water alone was removed from the system, thereby formulating a toluene solution containing sodium phenolate.

In tandem with the aforesaid reaction, a mixture of 0.15 mol (16.5 g) of resorcinol, 1.0 mol (94.1 g) of phenol, 1.3 mol (31.1 g) of lithium hydroxide, 52 g of water, and 600 mL of toluene was heated and refluxed in a 2L-capacity four neck flask, and water alone was removed from the system, thereby formulating a toluene solution containing resorcinol and a lithium salt of phenol. To this toluene solution was added drop by drop 580 g of a 20% by weight chlorobenzene solution that contained 1.0 unit mol (115.9 g) of dichlorophosphazene oligomers (62% by weight of a trimer, 12% by weight of a tetramer, 11% by weight of a pentamer and hexamer, 3% by weight of a heptamer, 12% by weight of oligomers having eight or more repeating units) at 30°C or below under stirring, and the mixture was stirred and reacted for 3 hours at 110°C. To the reaction mixture was added the aforesaid toluene solution containing sodium phenolate, and the reaction was continued for 4 hours at 110°C.



After the reaction was completed, the reaction mixture was washed three times with 1.0 L of a 3% by weight sodium hydroxide aqueous /19 solution and then washed three times with 1.0 L of water, after which the organic layer was concentrated under reduced pressure. The resulting product was heated and vacuum-dried for 11 hours at 80°C and 400 Pa or less, thereby obtaining 209 g of a white powder.

The obtained crosslinked phenoxyphosphazene compound had a hydrolyzed chlorine content of 0.08% by weight and a weight-average molecular weight (MW) of 1080, in terms of polystyrene equivalent (determined by GPC analysis), and, based on the phosphorus content and the values of CHN elemental analysis, the composition of the final product was found to be  $[N=(-O-m-Ph-O-)_{0.15}(-O-Ph)_{1.7}]$ . With TG/DTA analysis, the product did not show any clear melting point, but its decomposition initiating temperature was found to be 304°C and 5% weight-loss temperature 311°C. A quantitative analysis of the residual hydroxyl groups was conducted by an acetylation method, and, as a result, the amount was found to be below the detection limit ( $1 \times 10^{-6}$  equivalent/g or less, in terms of hydroxy equivalent per 1 g of a sample).

Synthesis Example 4 [Synthesis of Phenoxyphosphazene Compound (B-4) Having a Crosslinking Structure with the Use of 2,2-bis(p-oxyphenyl) isopropylidene group]

Into a 1 L-capacity four-neck flask that held 0.7 mol (65.9 g) of phenol and 500 mL of toluene was charged, under stirring, 0.65 gram

atom (14.9 g) of finely cut metal sodium while the liquid temperature inside the flask was maintained at 25°C. After the charging, the mixture was stirred for 8 hours at a temperature of from 77 to 113°C until the metal sodium disappeared completely.

In tandem with the aforesaid reaction, 1.6 gram atom (11.1 g) of finely cut metal lithium was charged, under stirring, into a 3 L-capacity four-neck flask that held 0.25 mol (57.1 g) of bisphenol A, 1.1 mol (103.5 g) of phenol, and 800 mL of tetrahydrofuran (THF) while the liquid temperature inside the flask was maintained at 25°C or below. After the charging, the mixture was stirred for 8 hours at a temperature of from 61 to 68°C until the metal lithium disappeared completely. To this slurry solution was added drop by drop, under stirring, 1.0 unit mol (115.9 g) of dichlorophosphazene oligomers (concentration: 37% by weight; chlorobenzene solution: 313 g, composition: 75% by weight of a trimer, 17% by weight of a tetramer, 6% by weight of a pentamer and hexamer, 1% by weight of a heptamer, and 1% by weight of oligomers having eight or more repeating units) over the course of 1 hour while the liquid temperature inside the flask was maintained at 20°C or below, and the mixture was reacted for 2 hours at 80°C. Thereafter, while the reaction system was stirred and the liquid temperature inside the flask was maintained at 20°C, the aforesaid sodium phenolate solution prepared separately was /20 added over the course of 1 hour, and the mixture was reacted at 80°C for 5 hours.

After the completion of the reaction, the reaction mixture was concentrated, thereby eliminating THF, and 1L of toluene was further added. This toluene solution was washed three times with 1 L of 2% by weight NaOH aqueous solution and subsequently washed three times with 1.0 L of water, after which the organic layer was concentrated under reduced pressure. The resulting product was heated and vacuum-dried for 11 hours at 80°C and 400 Pa or less, thereby obtaining 229 g of a white powder.

The obtained crosslinked phenoxyphosphazene compound had a hydrolyzed chlorine content of 0.07% by weight, and, based on the phosphorus content and the values of CHN elemental analysis, the composition of the final product was found to be  $[N=P(-O-Ph-C(CH_3)_2-Ph-O-)]_{0.25}(-O-Ph)_{1.50}]$ . Its weight-average molecular weight (Mw) was 1130, in terms of polystyrene equivalent (determined by GPC analysis). With TG/DTA analysis, the product did not show any clear melting point, but its decomposition initiating temperature was found to be 308°C and 5% weight-loss temperature 313°C. A quantitative analysis of the residual hydroxyl groups was conducted by an acetylation method, and, as a result, the amount was found to be below the detection limit ( $1 \times 10^{-6}$  equivalent/g or less, in terms of hydroxy equivalent per 1 g of a sample).

Synthesis Example 5 [Synthesis of Phenoxyphosphazene Compound (B-5) Having a Crosslinking Structure with the Use of 4,4'-sulfonyl diphenylene (bisphenol-S residue)]

Into a 1 L-capacity four-neck flask that held 0.4 mol (37.6 g) of phenol and 500 mL of THF was charged, under stirring, 0.4 gram atom (9.2 g) of finely cut metal sodium while the liquid temperature inside the flask was maintained at 25°C. After the charging, the mixture was stirred for 5 hours at a temperature of from 65 to 72°C until the metal sodium disappeared completely.

In tandem with the aforesaid reaction, 1.8 gram atom (41.4 g) of metal lithium was charged, at 25°C or below, into a 1 L-capacity four-neck flask that held 500 mL of a tetrahydrofuran (THF) solution that contained 1.70 mol (160.0 g) of phenol and 0.05 mol (12.5 g) of bisphenol-S. After the charging, the temperature was raised to 61°C over the course of 1 hour, and the stirring was continued for 6 hours at a temperature of from 61 to 68°C, thereby formulating a sodium phenolate mixture solution. This solution was added drop by drop to 580 g of a 20% by weight chlorobenzene solution that contained 1.0 unit mol (115.9 g) of dichlorophosphazene oligomers (a mixture of 62% /21 by weight of a trimer, 12% by weight of a tetramer, 11% by weight of a pentamer and hexamer, 3% by weight of a heptamer, 12% by weight of oligomers having eight or more repeating units) under stirring while the mixture was cooled to 25°C or lower, and the reaction was carried out for 5 hours at 71 to 73°C under stirring. Thereafter, the aforesaid sodium phenolate mixture solution prepared earlier was added drop by drop, and the reaction was continued at 71 to 73°C for 3 hours.

After the completion of the reaction, the reaction mixture was concentrated, redissolved in 500 mL of chlorobenzene, washed three times with a 5% by weight NaOH aqueous solution, washed with 5% by weight sulfuric acid, washed with a 5% by weight sodium hydrogen carbonate aqueous solution, washed three times with water, and concentrated to dryness, thereby obtaining 218 g of a light yellow wax-like product.

The obtained crosslinked phenoxyphosphazene compound had a hydrolyzed chlorine content of 0.01% by weight or less, and, based on the phosphorus content and the values of CHN elemental analysis, the composition of this product was found to be roughly  $[N=P(-O-Ph-SO_2-Ph-O-)_{0.05}(-O-Ph)_{1.90}]$ . Its weight-average molecular weight (Mw) was 1080, in terms of polystyrene equivalent. With TG/DTA analysis, the product was found to have a melting point of 103°C, a decomposition initiating temperature of 320°C, and a 5% weight-loss temperature of 334°C. A quantitative analysis of the residual hydroxyl groups was conducted by an acetylation method, and, as a result, the amount was found to be below the detection limit ( $1 \times 10^{-6}$  equivalent/g or less, in terms of hydroxy equivalent per 1 g of a sample).

Working Examples 1 through 15 and Comparative Examples 1 through

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Polyalkylene terephthalates A were combined with phosphazene compounds B, phenol resins C, other flame retardants D, carbonizable resins E, antioxidants/thermal stabilizers F, drip inhibitors G,

fillers H, and so on in the proportions shown in Tables 1 and 2, and the mixtures were kneaded at 240°C (in Examples 1 to 6, 8 to 9, 13 to 15, and Comparative Examples 1 to 8 and 10) or at 270°C (in Example 7 and Comparative Example 9, in which polycarbonate was added, and Examples 10 to 12 and Comparative Example 11, in which polyethylene terephthalate was added) for 5 minutes with the use of a Laboplastmill (a product of Toyo Seiki Co.), thereby obtaining compositions. These polyalkylene terephthalate-based resin compositions were injection-molded with a small-size molding machine, thereby preparing molded articles (77 mm x 9.5 mm x 3 mm) for flame retardancy test use. The flame retardancy of the molded articles was evaluated according to UL 94.

The results are shown in Tables 1 through 4.

TABLE 1

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	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6
ポリアリレート樹脂A 重量部	A-1 100	A-1 100	A-1 100	A-1 100	A-1 100	A-1 100
ホスファゼン化合物B 重量部	B-1 20	B-2 15	B-3 15	B-4 15	B-5 20	B-5 15
フェノール系樹脂C 重量部	C-1 15	C-1 15	C-2 15	C-2 15	C-2 15	C-2 15
他の難燃剤D 重量部	—	D-1 7	D-1 7	D-1 7	—	D-1 7
炭化性樹脂E 重量部	—	—	—	—	—	—
酸化防止剤/熱安定剤F 重量部	F-1 0.15	F-1 F-2 0.15 0.15	F-1 F-3 0.15 0.15	F-1 F-3 0.15 0.15	F-1 F-2 0.15 0.15	F-1 F-3 0.15 0.15
ドリップ防止剤G 重量部	G-1 0.7	G-1 0.7	G-1 0.7	G-1 0.7	G-1 0.7	G-1 0.7
充填剤H 重量部	—	—	—	—	—	—
UL94燃焼試験	V-1	V-0	V-0	V-0	V-1	V-0

Key: A) polyalkylene terephthalate resins A, parts by weight; B) phosphazene compounds B, parts by weight; C) phenol resins C, parts by weight; D) other flame retardants, parts by weight; E) carbonizable resins E, parts by weight; F) antioxidants/thermal stabilizers F, parts by weight; G) drip inhibitors F, parts by weight; H) fillers H, parts by weight; UL94 flame retardancy test; 1 through 6) working example.

TABLE 2

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	実施例 7	実施例 8	実施例 9	実施例 10	実施例 11	実施例 12	実施例 13	実施例 14	実施例 15
ポリメタクリレート樹脂A 重量部	A-1 100	A-2 100	A-2 100	A-3 100	A-1 A-3 70 30	A-2 A- 3 70 30	A-2 100	A-2 100	A-2 100
ホスファゼン化合物B 重量部	B-5 20	B-3 20	B-5 20	B-3 15	B-5 15	B-5 20	B-5 10	B-5 20	B-5 20
フェノール系樹脂C 重量部	C-2 10	C-2 20	C-2 20	C-2 15	C-2 15	C-2 20	C-3 20	C-4 15	C-5 20
他の難燃剤D 重量部	D-1 10	D-1 10	D-1 10	D-1 7	D-1 7	D-1 10	D-1 0- 2 10 10	D-3 10	D-1 10
炭化性樹脂E 重量部	E-1 30	—	—	—	—	—	—	E-2 5	—
酸化防止剤/熱安定剤F 重量部	F-1 F-3 0.2 0.2	F-1 F-3 0.2 0.2	F-1 F-3 0.2 0.2	F-1 F-3 0.2 0.2	F-1 F-3 0.15 0.15	F-1 F- 3 0.2 0.2	F-1 0.2	F-1 0.2	F-1 0.2
ドリップ防止剤G 重量部	G-1 1.0	G-1 1.0	G-1 1.0	G-1 1.0	G-1 1.0	G-1 1.0	—	G-1 1.0	G-1 1.0
充填剤H 重量部	—	H-1 65	H-1 65	—	—	H-1 65	H-1 65	H-1 65	H-1 65
UL94燃焼試験	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0

Key: A) polyalkylene terephthalate resins A, parts by weight; B) phosphazene compounds B, parts by weight; C) phenol resins C, parts by weight; D) other flame retardants, parts by weight; E) carbonizable resins E, parts by weight; F) antioxidants/thermal stabilizers F, parts by weight; G) drip inhibitors F, parts by weight; H) fillers H, parts by weight; UL94 flame retardancy test; 7 through 15) working example.



TABLE 3

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	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5	比較例 6
ポリアリレート樹脂A 重量部	A-1 100	A-1 100	A-1 100	A-1 100	A-1 100	A-1 100
ホスファゼン化合物B 重量部	—	B-1 15	B-2 15	B-3 15	B-4 15	B-5 15
フェノール系樹脂C 重量部	—	—	—	—	—	—
他の難燃剤D 重量部	—	—	—	—	—	—
炭化性樹脂E 重量部	—	—	—	—	—	—
酸化防止剤/熱安定剤F 重量部	F-1 0.15	F-1 0.15	F-1 F-2 0.15 0.15	F-1 F-3 0.15 0.15	F-1 F-3 0.15 0.15	F-1 F-3 0.15 0.15
ドリップピング防止剤G 重量部	G-1 0.7	G-1 0.7	G-1 0.7	G-1 0.7	G-1 0.7	G-1 0.7
充填剤H 重量部	—	—	—	—	—	—
UL94燃焼試験	HB以下	HB以下	HB以下	HB以下	HB以下	HB以下

Key: A) polyalkylene terephthalate resins A, parts by weight; B) phosphazene compounds B, parts by weight; C) phenol resins C, parts by weight; D) other flame retardants, parts by weight; E) carbonizable resins E, parts by weight; F) antioxidants/thermal stabilizers F, parts by weight; G) drip inhibitors F, parts by weight; H) fillers H, parts by weight; UL94 flame retardancy test; 1 through 6) comparative example.

TABLE 4

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	比較例 7	比較例 8	比較例 9	比較例 10	比較例 11
ポリアリレート樹脂A 重量部	A-1 100	A-1 100	A-1 100	A-2 100	A-3 100
ホスファゼン化合物B 重量部	—	—	—	—	—
フェノール系樹脂C 重量部	C-2 15	C-2 15	C-2 10	C-2 20	C-2 15
他の難燃剤D 重量部	—	D-1 7	D-1 10	D-1 10	D-1 7
炭化性樹脂E 重量部	—	—	E-1 30	—	—
酸化防止剤/熱安定剤F 重量部	F-1 F-3 0.15 0.15	F-1 F-3 0.15 0.15	F-1 F-3 0.2 0.2	F-1 F-3 0.2 0.2	F-1 F-3 0.2 0.2
ドリップング防止剤G 重量部	G-1 1.0	G-1 1.0	G-1 1.0	G-1 1.0	G-1 1.0
充填剤H 重量部	—	—	—	H-1 65	—
UL94 燃焼試験	HB以下	HB以下	HB以下	HB以下	HB以下

Key: A) polyalkylene terephthalate resins A, parts by weight; B) phosphazene compounds B, parts by weight; C) phenol resins C, parts by weight; D) other flame retardants, parts by weight; E) carbonizable resins E, parts by weight; F) antioxidants/thermal stabilizers F, parts by weight; G) drip inhibitors F, parts by weight; H) fillers H, parts by weight; UL94 flame retardancy test; 7 through 11) comparative example.

As can be seen from Tables 1 to 4, the polyalkylene terephthalates of the Working Examples were rendered highly flame retardant.

Working Examples 16 through 19 and Comparative Example 12

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Polyalkylene terephthalates A were combined with phosphazene compounds B, phenol resins C, other flame retardants D, carbonizable resins E, antioxidants/thermal stabilizers F, drip inhibitors G, fillers H, and so forth in the proportions shown in Table 5, and the mixtures were extruded with a 30 $\Phi$  [translator's note:  $\Phi$  indicates the diameter, but the unit is missing here] twin extruder (TEX30, a product of The Japan Steel Works, Ltd.), thereby preparing compositions in pellet form. Thereafter, using an 80-ton molding machine, formed articles to be used for various tests were prepared from the obtained pellet-form compositions, and flame retardancy, a property (tensile property), and an odor generated during the molding process were evaluated according to the following methods.

(Flame Retardancy)

Flame retardancy was evaluated in accordance with UL-94, using 1.6 mm-thick test pieces

(Tensile Property)

In accordance with ASTM D-790, bending strength was determined using test pieces obtained by injection molding.

(Evaluation of Odor Level During Molding)

The following three levels were used to evaluate the odor level of each test sample.

O: Little odor

$\Delta$ : Slight odor

X: Strong odor.

The results are shown in Table 5.

TABLE 5

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	実施例 16	実施例 17	実施例 18	実施例 19	比較例 12
ポリアルキレナテラフタレート樹脂A 重量部	A-1 100	A-1 100	A-2 100	A-2 A-3 50 50	A-2 100
ホスファゼン化合物B 重量部	B-5 15	B-5 20	B-5 25	B-5 23	—
フェノール系樹脂C 重量部	C-3 15	C-2 20	C-3 25	C-3 23	C-6 20
他の難燃剤D 重量部	D-1 7	D-1 10	D-1 12	D-1 12	D-2 20
炭化性樹脂E 重量部	—	E-1 40	—	—	—
酸化防止剤/熱安定剤F 重量部	F-1 F-3 0.2 0.2	F-1 F-4 0.2 0.1	F-1 0.3	F-1 F-3 0.7 0.7	F-1 0.3
ドリップピング防止剤G 重量部	G-1 0.7	G-1 1.0	G-1 1.0	G-1 1.0	G-1 1.0
充填剤H 重量部	—	—	H-1 70	H-2 70	H-1 60
UL94 燃焼試験	V-0	V-0	V-0	V-0	V-1
TS MPa	57	62	115	122	112
FS MPa	94	101	159	170	155
成形時の臭気(K)	○	△	○	○	×

Key: A) polyalkylene terephthalate resins A, parts by weight; B) phosphazene compounds B, parts by weight; C) phenol resins C, parts by weight; D) other flame retardants, parts by weight; E) carbonizable resins E, parts by weight; F) antioxidants/thermal stabilizers F, parts by weight; G) drip inhibitors F, parts by weight; H) fillers H, parts by weight; UL94 flame retardancy test; K) odor during molding; 16 through 19) working example; 12) comparative example.

As is evident from Table 5, the polyalkylene terephthalates of the Working Examples were rendered highly flame retardant without losing their excellent properties. Furthermore, they do not produce

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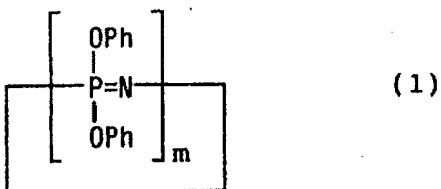
much odor during molding, thus rendering themselves excellent for work environment consideration.

# CLAIMS

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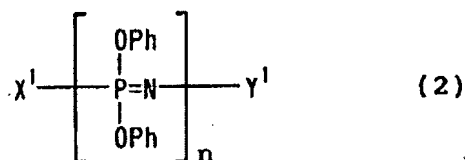
1. A flame-retardant resin composition comprising a flame retardant that contains a phosphazene compound and a phenol resin and a polyalkylene terephthalate resin, the phosphazene compound being a minimum of one kind selected from a group consisting of (1) cyclic phenoxyphosphazene compounds, (2) linear phenoxyphosphazene-compound, and (3) crosslinked phenoxyphosphazene compounds presented in the following:

(1) cyclic phenoxyphosphazene compounds:



(wherein m is an integer of 3 to 25, and Ph denotes a phenyl group),

(2) linear phenoxyphosphazene compounds



[wherein X<sup>1</sup> represents the group -N=P(OPh)<sub>3</sub> or the group -N=P(O)OPh; Y<sup>1</sup> represents the group -P(OPh)<sub>4</sub> or the group -P(O)(OPh)<sub>2</sub>; n is an integer of 3 to 10,000; and Ph has the same meaning as defined for the aforesaid formula (1)], and

(3) crosslinked phenoxyphosphazene compounds that are formed by crosslinking a minimum of one kind of phenoxyphosphazene compound selected from the cyclic phenoxyphosphazene compounds (1) and linear phenoxyphosphazene compounds (2) with a minimum of one kind of crosslinking group selected from a group consisting of an o-phenylene group, m-phenylene group, p-phenylene group, and bisphenylene group that is represented by formula (3a):



[wherein A represents  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{SO}_2-$ ,  $-\text{S}-$ , or  $-\text{O}-$ , and a denotes 0 or 1], the proportion of said crosslinking groups being, in terms of the /30 phenyl groups, 0.1 to 50 mol % based on the total number of the phenyl groups in the phenoxyphosphazene compounds (1) and (2).

2. A resin composition according to Claim 1, wherein the polyalkylene terephthalate resin comprises a polyethylene terephthalate resin or a polybutylene terephthalate resin.

3. A resin composition according to Claim 1, wherein the phenol resin comprises a minimum of one kind selected from a group consisting of phenol novolak resins, phenol aralkyl resins, and polyvinyl phenol resins.

4. A resin composition according to Claim 3, wherein the phenol aralkyl resin comprises a reaction product of a phenol and an aralkyl compound, and the polyvinyl phenol resin comprises a homopolymer of a

polyvinyl phenol or a copolymer of a polyvinyl phenol and a copolymerizable monomer.

5. A resin composition according to Claim 3, wherein the phenol novolak resin comprises a minimum of one kind selected from a group consisting of (a) a random phenol novolak resin, (b) a high-ortho phenol novolak resin, (c) a triazine-modified phenol novolak resin, and (d) a phenol novolak resin containing a free monomer component and/or a dimer component only in small amounts.

6. A resin composition according to Claim 3, wherein the phenol novolak resin comprises a phenol novolak resin in which the total amount of the free monomer component and dimer component is not more than 20% by weight of the resin as a whole.

7. A resin composition according to Claim 1, wherein the flame retardant contains the phosphazene compound and the phenol resin in a proportion of the former/the latter=5/95 to 95/5 (weight ratio).

8. A resin composition according to Claim 1, wherein the proportion of the flame retardant is from 1 to 100 parts by weight per 100 parts by weight of the polyalkylene terephthalate resin.

9. A flame-retardant resin composition comprising a flame retardant that contains a phenol resin and the phosphazene compound stated in Claim 1 and a polyalkylene terephthalate resin, wherein the aforesaid phenol resin comprises a minimum of one kind selected from a group consisting of phenol novolak resins, phenol aralkyl resins, and polyvinyl phenol resins, wherein the flame retardant contains the

phosphazene compound and phenol resin in a proportion of the /31  
former/the latter=20/80 to 80/20 (weight ratio), and wherein the  
proportion of the aforesaid flame retardant is from 5 to 90 parts by  
weight per 100 parts by weight of the polyalkylene terephthalate resin.

10. A resin composition according to Claim 1 or 9, which further  
comprises a minimum of one kind selected from a group consisting of  
nitrogen-containing flame retardants, phosphate-based flame retardants,  
and carbonizable resins.

11. A resin composition according to Claim 10, wherein the  
nitrogen-containing flame retardants comprise a minimum of one kind  
selected from a group consisting of melamine or derivatives thereof,  
melamine condensates, cyanurates of melamine or derivatives thereof,  
and salts of pyrophosphoric acid or a polyphosphoric acid with  
triazine derivatives.

12. A resin composition according to Claim 10, wherein the  
phosphate-based flame retardant comprises a minimum of one kind  
selected from a group consisting of phosphates and polyphosphates.

13. A resin composition according to Claim 10, wherein the  
carbonizable resin comprises a minimum of one kind selected from a  
group consisting of polycarbonate resins, polyarylate resins, aromatic  
epoxy resins, polyphenylene oxide resins, and polyphenylene sulfide  
resins.



14. A resin composition according to Claim 1 or 9, which further comprises a minimum of one kind selected from a group consisting of antioxidants, thermal stabilizers, drip inhibitors, and fillers.

15. A process for producing a flame-retardant resin composition, said process comprising mixing a polyalkylene terephthalate resin and the flame retardant stated in Claim 1.

16. A molded article formed from the flame-retardant resin composition stated in Claim 1.